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⑩ **CANADIAN PATENT**

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⑤4 **FOAMED SHEET MATERIAL AND PROCESS OF PREPARATION**

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No. OF CLAIMS 15 - No drawing

This invention relates to extrusion of extrudable resinous substances.

More particularly, this invention relates to a novel method of producing foamed extrudable resinous substances, and a novel foamed product.

Single and multi-layer foamed products per se are known in the art. Such products are normally produced by what may be termed a "calendaring" method or variations of this type of operation, where a layer of preformed foamed resin in the form of a sheet or film is employed. In variations of this method, the foamed resin may be laid down on a layer of substrate material or in other methods, may be sandwiched between two layers of a substrate resin. In some cases, the resinous substrate is adhesively bonded to the foamed core and in other cases, the foamed core is united to the inner and/or outer substrate layers or "skins" by additional treatments involving heat and/or pressure. Typical prior art references showing the production of foamed material by such methods are shown in United States Patent 3,220,902 and Canadian Patents 792,216, 792,649, etc.

The production of foamed products by the prior art methods of calendaring or by cast film technology is, within its own rights, adequate to produce various types of articles. However, relatively expensive equipment is required to do this particularly where the foamed material is sandwiched between inner and/or outer layers of a substrate or skin in that in addition to the usual equipment, other components such as heaters, pressure rollers, etc. are required. Moreover, the control of the stretch of the foamed material is somewhat difficult and, it would be desirable if a simpler method of producing such products were obtainable.



The use of foamed products finds application in many different areas and their use is expanding year by year. For example, rigid and semi-rigid foams find extensive use in auto-padding, for insulation purposes in the construction industry, as well as in various appliances and containers. In the field of flexible foams, extensive use is found in residential or industrial building construction as vapour barriers and thermal insulation.

10 With the present invention, applicant has developed a novel method of producing foamed materials whereby the desired degree of stretching and thickness of the foamed product may be readily controlled without additional equipment. In fact, equipment in use today may be employed in the method of the present invention.

In accordance with one aspect of the present invention, there is provided a method of producing a foamed sheet material including the steps of providing a first source of an extrudable, flowable, foamable resin, providing at least one further source of an extrudable, flowable resin, forming one
20 of said resin sources into a first molten resinous flow stream of said resin, forming the other of said resin sources as a further molten resinous flow stream in juxtaposition with said first flow stream to form a combined first and further molten flow streams, coextruding said combined molten flow streams as a laminar flow, and permitting said one foamable stream to foam to a desired degree thereby to form foamed sheet resin material having a resinous skin on a foamed layer.

The method of the present invention may be carried out in equipment commercially available for making unfoamed
30 sheeting and film without the necessity of having additional components normally associated with the production of foamed

sheet materials. More particularly, the invention of the present method may be carried out by extruding the sources of material, as a laminate, in coextrusion devices known in the art as either a flat die or a circular die coextrusion apparatus. Flat coextrusion dies are illustrated in, for example, United States Patent 3,320,636 (H.A. Corbett); circular coextrusion dies of the type which may be used with the present invention are those illustrated in, for example, United States Patent 3,266,093 (H.A. Corbett).

10 In carrying out the method of the present invention, one or more layers of foamed resinous material may be coextruded with one or more layers of unfoamed resinous material to form a foamed sheet product having at least one foamed resinous layer in juxtaposition with at least one unfoamed resinous layer, with the unfoamed layer forming a skin about the foamed layer.

 In accordance with preferred embodiments of the present invention, applicant's method may be employed to produce multi-layered foamed products in which a layer of foam may be
20 encompassed between outer skins of unfoamed material; in other embodiments, there may be provided two or more layers of foamed material, optionally separated by one or more layers of unfoamed material, which may be provided with at least one outer layer of unfoamed material. Thus, as will be seen, the method of the present invention permits the production of a wide variety of materials in which unfoamed and foamed layers of a different or similar nature may be employed to produce a foamed product having variable properties according to desired requirements. Moreover, the thickness of the unfoamed and foamed layers may
30 vary as desired again to vary the required characteristics of a product.

 The foamed layer or core of the products may be of

any suitable foamable resin capable of being extruded by either the flat die or circular die coextrusion procedures; which resin is provided with compatible foaming and/or flowing agents therein in an amount sufficient to cause foaming of the resin. Typical resins which may be employed are the thermoplastic resins such as the polyolefins, the vinyl type resins and ionomeric polymers. Representative of the polyolefins are polypropylene, polyethylene, copolymers of propylene and other monomers, e.g. polypropylene copolymers containing vinyl comonomer (typically in amounts up to 30% of the latter), and copolymers of ethylene and other comonomers, e.g. vinyl acetate (typically in an amount up to about 30%). Representative of the vinyl type resins are polyvinyl chloride, copolymers of vinyl chloride and vinylidene chloride and copolymers of vinyl chloride and acrylic acid. Representative of the ionomeric polymers are the metal salts of a copolymer of ethylene and acrylic acid. Applicant has found that polyethylene in various densities - e.g. low density (.910 to .925), medium density (.926 to .940) and high density polyethylene (.941 to .965) may be employed in the process of the present invention to produce superior foam products which are economical due to the ready availability of polyethylene.

In carrying out the process of the present invention, the polymer or copolymer which will form the foamed layer or core is provided with a suitable amount of the required compatible foaming or blowing agent which forms a gaseous phase above the melting temperature of the polymer. The compatible foaming agents are well known to those skilled in this art - for example, representative of the foaming agents for polyolefins are azodicarbonamide, azodiisobutyronitrile dinitroso-pentamethylenetetramine, and oxybis-(benzene sulphonyl hydrazide)

of which azodicarbonamide is preferred; in the case of a hydrophilic ionomeric polymer, water may normally be used as a foaming agent. The one or more layers of unfoamed resinous material may be the same or different as the foamed layers. Thus, the unfoamed layers may be any of the materials mentioned above, or any combination of such materials. A particularly preferred embodiment of the present invention is the provision of a foamed polyethylene core having unfoamed polyethylene skins on each major surface thereof.

10 Various other additives common to the thermoplastic art may also be incorporated into the polymers or copolymers employed as the foamed layer or core according to conventional expedients - e.g. colouring agent, fire retardants, etc. Similarly, one or more layers of non-foamed material may likewise include such conventional additives in addition to others e.g. slip additives, antiblock additives, etc.

 During the coextrusion process of the present invention the resin having the foaming agent therein is preferably extruded in a substantially unfoamed condition whereafter,
20 following extrusion, the polymer or copolymer is permitted to foam to the desired degree of expansion. The desired degree of foaming and hence expansion may be obtained by selection of the suitable blowing agent and by controlling the cooling rate of the coextruded structure - i.e. the rate at which the structure is cooled is controlled to allow sufficient time for the foamed layer or core of the laminate to expand to the proper extent yielding the desired cell structure of the product.

 Applicant has found that structures having a foamed
30 layer or core may be coextruded in which the thickness of such a layer may vary between 2 mils to 1 inch or more. In case of a very thin product, the foaming reaction is stopped by

suitable means immediately upon extrusion from a coextrusion die, or for a greater thickness by cooling a distance removed from the point of extrusion. Cooling of the foamed structure may be accomplished in several ways according to conventional cooling techniques used in the blown tube method of producing film, e.g. by blowing air onto the structure at a rate sufficient to cool it, by running the structure over a cooling mandrel or by directly bringing the structure into contact with a cooling medium, e.g. water.

10 The thickness of each outer skin may vary according to the characteristics desired in the product - e.g. 0.2 mil to 10 mils or greater.

 In carrying out the method of the present invention using the flat coextrusion die or circular coextrusion die equipment, two or more extruders may be used to feed the die, each extruder supplying a different resinous material in either an unfoamable or foamable condition. In the case where a three-layered laminate is desired, with each layer being of a different material, three separate extruders will be employed
20 to feed three separate flow streams of the material; while in the case of a three-layered laminate in which, for example, the inner and outer skins sandwiching a foam core are the same, one extruder may feed the die for both the outer layers and a separate extruder may feed the die for the foamable material.

 Various types of extruders may be used in the method of the present invention, the use of the extruder being to supply a flow of molten material to the die in a flow stream at the desired rate of flow.

 When carrying out the invention using a circular
30 coextrusion die, the circular die will produce an annular tube which may be formed into an annular bubble according to the conventional practice in the blown tube method of film

production. The blown tube method of film production is well known in the art and reference may be had, for example, to Canadian Patent 460,963 illustrating such a method. Briefly summarized, the blown tube method involves the formation of an annular tube of molten material extruded from a die, whereafter by use of differential air pressure between the interior of the tube and the atmosphere the tube is maintained in an inflated condition and may be blown to a desired diameter. After the temperature of the tube is lowered below the melting point of the extruded material the tube is collapsed (for example between a pair of nip rollers) and optionally slit (to form sheet material in place of a tube) and wound on a wind-up roller.

In employing the coextrusion laminar method of the present invention, applicant has found that the laminated foam products produced are characterized by a degree of flexibility which can be carefully controlled within specific limits according to the characteristics required and desired in a given product. Thus, for example, the flexibility of the products is controlled by varying the stiffness characteristics of all or individual resins making up the laminate; in certain cases it may be desirable to provide a rigid foam product having a flexible outer layer or in other cases a flexible foam with flexible outer layers, all of which can be accomplished with the use of the present invention. Moreover, the process of this invention produces products which form discrete layers, but in which, depending on the particular resin used for the layers, will form an integral and inherent bond with the adjacent layer, when the coextruded resins are mutually adherent and compatible, independent of the foaming of one layer. In other cases, the degrees of adhesion will of course vary with the type of materials. The inventive process also has

the advantage that it produces coextruded laminates in a much more simple manner as compared to prior art processes, resulting in large economies. Moreover, the products of the present invention have the advantage that they possess reduced fire hazard properties due to the particular way in which the foam is enclosed on one or both sides, compared to open foam products. Applicant has also found that due to the external or outer layers, cross-linking of the foam to the same extent as in the prior art foamed products is not necessary to the same degree to impart the required strength characteristics to the foam.

Still further, the provision of smooth external outer layers has many advantageous features over a similar product possessing only a rough foam surface, providing utility of such products in fields which require such characteristics.

The products of the present invention find use in automobile padding, thermal insulation in the construction field and appliance field, as well as containers. A particularly advantageous use of the products of the present invention is in the manufacture of light-weight container bags for conveying commodities, and in the installation of flexible foams, e.g. polyethylene foams, for lining of buildings and vapour barrier and thermal insulation purposes.

Having thus generally described the invention, reference will now be made to the following Example illustrating a preferred embodiment thereof.

EXAMPLE

This Example shows the production of a three-layered laminate consisting of a polyethylene foam inner core having outer surfaces of unfoamed polyethylene.

An extrusion device of the type illustrated in United States Patent 3,320,636, which is a flat extrusion die,

was employed. Two separate extruders were also connected to the die, one extruder feeding the inner and outer die apertures, the other feeding the die aperture which was adapted to form a central flow stream.

The first extruder was fed with low density polyethylene, the other one with low density polyethylene provided with a foaming agent (azodicarbonamide). The apparatus used was also provided with a wind-up roll and chill (cooling) rollers over which the coextruded product was passed.

10 The extruders were then operated to extrude the foamed polyethylene encased on both major surfaces, with a layer of unfoamed polyethylene. The extrusion conditions were adjusted whereby the outside layers were extruded at a thickness of about 1.5 mils. The cooling rollers were adjusted to permit the foam to expand to a thickness of approximately one-eighth inch whereafter the coextruded laminated foamed product was placed in contact with the cooling rollers to stop foaming, and after cooling the resulting structure was wound on a spool.

20 Examination of the product produced revealed that the inner and outer skins of polyethylene were inherently and integrally united to the foamed polyethylene core, and the product was found to have excellent flexibility characteristics.

Production of foam products by such a method provides a highly economical product since not only can the less expensive polymers or copolymers be used but also the equipment involved does not require any special modifications, etc.

It will be understood that various changes can be made to the above without departing from the spirit and scope of the invention.

permitting said foamable resin to foam to a desired thickness.

3. A method as defined in Claim 1 or 2, wherein the molten resins are extruded as an annular co-extruded tube and which includes the steps of forming said material into a co-extruded laminar flow of materials as a tube by the blown tube process utilizing a differential air pressure between the inside of said tube and the atmosphere, allowing the foamable resin of the co-extruded laminar material to foam to a desired thickness outside said die, cooling said material after said foamable resin has expanded to a desired degree and thereafter collapsing said cooled tube.

4. A method as defined in Claim 1, wherein the resinous materials are co-extruded from a flat die to form a single flat co-extruded laminar sheet, and which includes the step of cooling the molten co-extruded resinous laminar material after said foamable layer has foamed to a desired degree.

5. A method as defined in Claim 1 or 2, wherein said foamable material is selected from the group consisting of copolymers and polymers of polyolefins, ionomeric polymers and vinyl chloride polymers and copolymers.

6. A method as defined in Claim 2, wherein said foamable material is a polyolefin selected from the group consisting of polyethylene polymers and copolymers, and polypropylene polymers and copolymers.

7. A method as defined in Claim 2 or 6, wherein said inner and outer resinous layers are selected from the group consisting of polyethylene polymers and copolymers and polypropylene polymers and copolymers.

8. A method as defined in Claim 2, wherein the material extruded is a three layered co-extruded laminate having a central layer of foamable material, said central layer having an extrudable unfoamed thermoplastic resin in juxtaposition therewith on either side thereof, said central layer and said thermoplastic resin being polyethylene polymer or copolymer.
9. A method as defined in Claim 2 or 8, wherein said central layer has a thickness of from about 2 mils to 1 inch and said inner and outer layers have a thickness of from about 0.2 mil to about 10 mils.
10. A one-piece seamless laminated co-extruded foamed sheet product having at least one foamed resinous layer of foamable material with at least one unfoamed non-foamable resinous layer in juxtaposition and integrally united therewith, said product having a continuous non-interrupted interface between said foamed layer and said unfoamed layer and said product having been co-extruded as a laminar flow.
11. The product of Claim 10 wherein said foamed product consists of a foamed core having two major faces, and unfoamed resinous layers in juxtaposition with each of said major faces.
12. The product of Claim 10 or 11, wherein said foamed material is selected from the group consisting of copolymers and polymers of polyolefins, ionomeric polymers and vinyl chloride polymers and copolymers.
13. The product of Claim 10 or 11, wherein said foamed material is a polyolefin selected from the group consisting of polyethylene polymers and copolymers, and polypropylene polymers and copolymers.

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14. The product of Claim 11, wherein said core and said resinous layers are all polyethylene.

15. The product of Claim 10 or 11, said product comprising a blown-tube co-extruded product.



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